

Isotopic Tracing of Fuel Components in Particulate Emissions from Diesel Engines using Accelerator Mass Spectrometry (AMS)

Bruce A. Buchholz, Charles J. Mueller, and John Garbak

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Bruce A. Buchholz (primary contact)
Center for Accelerator Mass Spectrometry, L397
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94551
(925) 422-1739; FAX: (925) 423-7884; email: buchholz2@llnl.gov

Charles J. Mueller
Combustion Research Facility
Sandia National Laboratory
Livermore, CA 94551

DOE Program Manager: John Garbak (202) 586 1723, fax: (202) 586 9811, e-mail:
John.Garbak@ee.doe.gov

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Objectives

- Determine contribution of diesel fuel components and oxygenates to soot formation.
- Separate volatile and non-volatile fractions of soot.
- Test combustion paradigm that all carbon and oxygen in fuel is equal.
- Produce data to validate combustion modeling.

Approach

- Construct filter assembly to collect exhaust soot.
- Analyze carbon isotope content of all fuel components and lubrication oil.
- Collect soot from skip fired 1.7L optical engine. Complete isotopic analyses of soot and determine contributions from available carbon sources.

Accomplishments

- Filter assembly constructed and in use.
- Preliminary tests completed to determine engine operation conditions for loading filters with sufficient soot for isotopic analyses.
- Determined lubrication oil leakage to be major contributor of carbon emissions from test engine.

Future Directions

- Determine contributions of major fuel components to soot production and test selected oxygenates.
- Collect gaseous emissions and separate major components.
- Obtain carbon-14 labeled lube oil and run it in conventional diesel engine. Determine contribution of lube oil to soot and CO₂ emissions.
- Apply tracing techniques to HCCI (homogeneously charged compression ignition) engines.

Introduction

Accelerator mass spectrometry (AMS) is an isotope-ratio measurement technique developed in the late 1970s for tracing long-lived radioisotopes (e.g., ¹⁴C half life = 5760 y). The technique counts individual nuclei rather than waiting for their radioactive decay, allowing measurement of more than 100 low-level ¹⁴C samples per day (Vogel et al, 1995). The LLNL AMS system is shown in Fig.1.

The contemporary quantity of ¹⁴C in living things (¹⁴C/C = 1.2x10⁻¹² or 110 fmol ¹⁴C/ g C) is highly elevated compared to the quantity of ¹⁴C in petroleum-derived products. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components in the emissions of an engine without the use of radioactive materials. If synthesis of a fuel component from biologically-derived source material is not feasible, another approach is to purchase ¹⁴C-labeled material (e.g., dibutyl maleate (DBM)) and dilute it with petroleum-derived material to yield a contemporary level of ¹⁴C. In each case, the virtual absence of ¹⁴C in petroleum based fuels gives a very low ¹⁴C background that makes this approach to tracing fuel components practical.

Regulatory pressure to significantly reduce the particulate emissions from diesel engines is driving research into understanding mechanisms of soot formation. If mechanisms are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest possible fuel components that can improve combustion and reduce PM emissions. The combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. AMS allows us to label specific fuel components, including oxygenates, trace the carbon atoms, and test this combustion modeling paradigm.

Volatile and non-volatile organic fractions (VOF, NVOF) in the PM can be further separated. The VOF of the PM can be oxidized with catalysts in the exhaust stream to further decrease PM. The effectiveness of exhaust stream catalysts to oxidize products from tracer fuel components can be monitored through AMS measurement of carbon in PM.

Approach

The ¹⁴C concentration of all fuel components and the lubrication oil were checked by AMS and confirmed to be of petroleum origin (¹⁴C/C ratios ~10⁻¹⁵). A test fuel containing 88% DBM, 7% n-hexadecane (NHD) and 5% ethylhexyl nitrate (EHN) was spiked with labeled DBM to obtain fuel containing 78 fmol ¹⁴C/ g C, approximately 70% the ¹⁴C found in living things.

Pre-combusted quartz filters were loaded with PM drawn from the exhaust manifold of a modern-technology, 4-stroke, heavy-duty DI diesel engine that has been modified to provide extensive optical access into the combustion chamber. Injection timing was optimized such that the engine produced maximum gross indicated torque. The engine operated at 1200-rpm and moderate load (8.00 bar gross indicated mean effective pressure (gIMEP)). The optical engine run in skip fire mode (fire every 12th cycle) required 48 fires to deposit sufficient soot for isotopic analysis (see figure 2). Filters were handled with stainless steel forceps and placed on aluminum foil after loading to avoid contamination with other carbon sources.

Some filters were baked at 340°C for 2 h to remove the VOF of soot. The remaining carbon on the filters was assumed to be NVOF. The procedure was developed using NIST SRM 2975 diesel soot to obtain consistent isotope ratios and mass fraction of the NVOF. SRM 2975 has a 7% VOF with this procedure. We expect a similar VOF from the optical engine since the soot is collected close to the exhaust manifold without using a dilution tunnel.

Results

All filters were loaded with a significant amount of carbon. We found lubrication oil deposition on the filters to be a major component of the carbon inventory. The lube oil deposition decreased over the course of a day, but the total carbon remained significant on filters collected with motored cycles only (see Fig. 3). The mass of carbon on filters collected with skip fires was no higher than those with motored cycles only.

The ¹⁴C content of the motored and skip fired samples is almost identical. Although the ¹⁴C concentration in the fuel is ~1000x that of the lube oil, the carbon mass on the filters is almost entirely due to lube oil. Removing the VOF from the filters produced a consistent carbon mass (Fig. 3), but the isotope content varied by a factor of six. The heating procedure to remove the VOF did not visibly reduce the deposited soot, indicating the non-combusted lube oil was substantially removed.

Conclusions

The large contribution of lubrication oil to the exhaust emissions, both as oil from non-fired cycles and as combusted soot, complicates quantitation of fuel components in PM. Results indicate that DBM contributes very little carbon to soot formation in this engine. It is impossible to separate the contributions of the other fuel components, NHD and EHN, from the lube oil due to their similar isotopic signatures. The lube oil signal needs to be reduced either by limiting leakage down the valves and into the cylinder or by removing non-combusted oil as part of sample pretreatment. The logical next step is to obtain labeled lubrication oil for use in this and a conventional engine and determine its contribution to PM emissions. Determining the contribution of lube oil to emissions is important for assessing viability of exhaust catalyst technology.

Reference

Vogel, J. S.; Turteltaub, K. W.; Finkel, R.; Nelson, D. E. (1995) Accelerator Mass Spectrometry - Isotope Quantification at Attomole Sensitivity. *Anal. Chem.* **67**, 353-9A. This work was performed

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Acronyms

^{14}C	carbon-14
AMS	accelerator mass spectrometry
DI	direct injection
EHN	ethylhexyl nitrate
gIMEP	gross indicated mean effective pressure
HCCI	homogeneously charged compression ignition
NIST	National Institute of Standards and Technology
NHD	normal hexadecane
NVOF	non-volatile organic fraction
PM	particulate matter
SRM	standard reference material
VOF	volatile organic fraction

Fig. 1. View of LLNL AMS system from above the high energy magnets. The shared facility annually measures 10,000 ^{14}C samples at precision to 0.8% and $^{14}\text{C}/\text{C}$ ratios as low as 1 part in 10^{15} .

Fig. 2 Quartz filters loaded with emissions from optical engine. The filters were loaded with the following engine operating conditions: (A) motored only without firing, 12x48 cycles, 0.2 mg C from lube oil; (B) motored with 48 skip fires, 12x48 cycles, 0.28 mg C from lube oil and soot; (C) motored with 96 skip fires, 2x12x48cycles, 0.61 mg C from lube oil and soot.

Fig. 3 Carbon mass deposited on motored (M) and skip fired (F) filters during a day of operation. The filters are listed on the x-axis in the order in which they were collected. The mass of carbon was normalized to 12x48 cycles for samples with different collection times. The NVOF carbon mass appeared to be consistent, suggesting the lube oil departed in the VOF.





